

November 28, 1895.

The LORD KELVIN, D.C.L., LL.D., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair, and the list of Officers and Council nominated for election was read as follows:—

President.—Sir Joseph Lister, Bart., F.R.C.S., D.C.L.

Treasurer.—Sir John Evans, K.C.B., D.C.L., LL.D.

Secretaries.—{ Professor Michael Foster, M.A., M.D.
The Lord Rayleigh, M.A., D.C.L.

Foreign Secretary.—Edward Frankland, D.C.L., LL.D.

Other Members of the Council.—William Crookes, F.C.S.; Sir Joseph Fayrer, K.C.S.I.; Lazarus Fletcher, M.A.; Walter Holbrook Gaskell, M.D.; William Huggins, D.C.L.; The Lord Kelvin, D.C.L.; Professor Alexander B. W. Kennedy, LL.D.; Professor Horace Lamb, M.A.; Professor Edwin Ray Lankester, M.A.; Professor Charles Lapworth, LL.D.; Major Percy Alexander MacMahon, R.A.; Professor John Henry Poynting, D.Sc.; Professor Arthur William Rücker, M.A.; Osbert Salvin, M.A.; Professor Harry Marshall Ward, D.Sc.; Admiral William James Lloyd Wharton, C.B.

The following Papers were read:—

- I. "The Expansion of Argon and of Helium as compared with that of Air and Hydrogen." By J. P. KUENEN, Ph.D., Professor of Physics in University College, Dundee, and W. W. RANDALL, Ph.D., Lecturer in Johns Hopkins University, Baltimore, U.S.A. Communicated by Professor RAMSAY, F.R.S. Received November 14, 1895.

Accurate comparisons of temperatures, as read with the aid of thermometers filled with different gases, have not often been made. The history of the subject may be said to have begun with the classical researches of Regnault.* Of recent work of this kind, that

* 'Relation des Expériences,' &c., 1847-62.

of Chappuis* was performed entirely at temperatures below 100° , the gases employed being hydrogen, nitrogen, and carbon dioxide. The experiments of Grunmach and Pernet† were also conducted at temperatures below 100° . Crafts‡ has compared the readings of a number of mercury thermometers with those obtained by Regnault and by himself with a hydrogen thermometer. Wiebe and Böttcher§ have determined the boiling points of a number of liquids in terms of the expansion of air.

In connexion with the work on argon and helium in progress at University College, it was suggested by Professor Ramsay that a comparison should be made between the readings shown by thermometers containing respectively argon, helium, hydrogen, and air. The temperatures used were: the melting point of ice and the boiling points of water, chlorbenzene, aniline, quinoline, and bromnaphthalene respectively. The gas to be experimented upon was contained in a bulb about 12 cm. long and 2.2 cm. wide, sealed at one end to a fine capillary tube about 12 cm. long; this, in turn, was connected with a piece of thick-walled glass tubing, having an inside diameter of about 0.2 cm. The wider tube was fitted with a stopcock, for convenience in filling the bulb, and at its lower end was connected with a stout rubber tube, which led to a movable mercury reservoir. Near the point at which the fine capillary tube was sealed to the wider tube, a mark was made on the latter: the mercury was always brought up to this mark in the experiments, and the difference of level in the tube and in the mercury reservoir was read off, with the aid of a telescope, from a glass scale graduated in millimetres, which stood directly behind the apparatus.

The bulb of the gas thermometer was heated in one of Ramsay and Young's vapour jackets, the mark on the stem being just below the cork closing the bottom of the jacket: consequently a small portion of the stem was not heated to the temperature of the vapour in the jacket. The error thus introduced was taken into account. No part of the mercury column which compressed the gas in the bulb was heated more than a few degrees above the temperature of the room, screens being employed to cut off radiation: the temperature of the mercury was, however, always determined as accurately as circumstances would permit, and the readings reduced to 0° . In order to protect the thermometer bulb from the effects of radiation, the jacket was shielded by an outer cylinder of thick pasteboard, with an air space between.

* 'Archives de Genève' [3], vol. 20, pp. 5—36, 153—179, 248—262; also 'Traité et Mémoires du Bureau International,' vol. 6.

† 'Metronomische Beiträge,' No. 3.

‡ 'Comptes Rendus,' vol. 95, pp. 836—839.

§ 'Zeitschrift für Instrumentenkunde,' vol. 10, pp. 16 and 233.

Since the mercury was always brought to the same point on the stem of the thermometer bulb, the volume of the gas, except for the change produced by the expansion of the glass, was in all the experiments the same, while the pressure was, of course, different for each temperature employed. For convenience, the bulb was filled, in the case of each gas, at from two-thirds to three-fourths atmospheric pressure: under these circumstances, the bulb was never subjected to an internal pressure greater than about $1\frac{1}{2}$ atmos.

Corrections.—All pressures were reduced to 0° . The coefficient of expansion of the glass of the bulb was carefully determined, and was found to be 0.00002804; its effect was allowed for. The effect of capillarity in depressing the mercury in the narrow tube was determined and taken into account. The volume of that part of the stem of the bulb which was not in the ice or vapour, as the case might be, was found to be 0.0003 of the whole, and was allowed for in the calculations. The change of volume in the bulb due to change of pressure was found to be negligible.

Gases.—The first gas experimented with was hydrogen. This was prepared from pure zinc, was washed with potassium permanganate solution and then with strong sulphuric acid, and was dried with phosphoric anhydride before it entered the previously exhausted bulb. The thermometer was successively filled and exhausted several times, in order to remove impurities, and was heated while vacuum to dislodge any gas clinging to the surface of the glass. Finally, the purified hydrogen was allowed to enter slowly until the required pressure was obtained.

Two sets of experiments were made with air. In the first set no effort was made to remove carbon dioxide, although the air was of course carefully dried. The readings were made by one of us alone, and, on account of the numerous details to be attended to which actually require the attention of two observers to be put beyond question, are probably not as accurate as the other series. The second series had to be brought to a close after the pressures corresponding to 0° and the boiling points of water and quinoline had been determined. In this series care was taken to use air free from carbon dioxide.

The helium used was some of that prepared and purified by Professor Ramsay. Its density was 2.13, that of oxygen being taken as 16.

The argon employed was prepared from atmospheric air by the method of Professor Ramsay. A large gas-holder was filled with air which had been slowly drawn through a long combustion tube filled with red-hot copper. This gas was dried, passed again over the hot copper, and then over red-hot magnesium shavings until absorption of nitrogen ceased. By these processes a gas was obtained consisting of about equal volumes of argon and nitrogen. Passage of this gas

backwards and forwards through tubes containing respectively red hot magnesium, red-hot copper oxide (to remove the hydrogen given off by the magnesium on heating), soda lime, and phosphoric anhydride, failed to remove the nitrogen completely. Finally, with the aid of a circulating apparatus,* which ensured the passage of all the gas over the hot magnesium, a product was obtained whose density was found to be 19·99, oxygen being 16. The thermometer was filled with this gas.

After the pressures exerted by the argon when the bulb was surrounded by melting ice and by the vapours of water, chlorbenzene, and aniline, successively, had been determined, the thermometer was heated in the vapour of quinoline, when, for some unknown reason, it cracked. A new bulb, of the same glass and as nearly as possible of the same size, was prepared, cleaned, and filled with argon, and a second series of readings made.

Finally, the argon was replaced by air, and the second series of readings for air, referred to above, begun. On account of the closing of the laboratory for the summer, this series was not carried as far as would have been desirable.

Temperatures.—The temperature of the jacket, when filled with steam from water boiling smoothly under atmospheric pressure, was taken from Kohlrausch's "Physical Measurements." The samples of the boiling liquids used were re-distilled, and were found to pass over without a rise in temperature of more than a tenth of a degree, in three cases; of a fifth of a degree in the fourth case.

| Kind of thermometer. | Corrected pressure. °. | In steam at about 100°, the temperature being accurately calculated. | Coefficient of expansion at constant volume, 0—100°. | Temperatures calculated. | | | |
|-------------------------|---------------------------|--|--|--------------------------|----------|------------|-------------------|
| | | | | Chlorbenzene. | Aniline. | Quinoline. | Brom-naphthalene. |
| 1. Hydrogen | — | 712·56 | — | 131·6 | 183·9 | 236·35 | — |
| 2. Air I. . . . | — | 737·74 | — | 131·8 | 183·6 | [234·9] | 281·65 |
| 3. Helium .. | 567·02 | 775·18 | 0·003665 | 132·2 | 184·1 | 236·9 | [278·3] |
| 4. Argon I.. | 517·02 | 706·06 | 0·003668 | 132·15 | 184·1 | — | — |
| 5. Argon II. | 529·54 | — | — | — | — | 237·8 | 281·5 |
| 6. Air II. . . | 511·68 | 698·79 | 0·003663 | — | — | 237·1 | — |
| Air (Wiebe) | — | — | 0·003670 | — | 184·3 | 235·9 | — |
| Temperature (R. and Y.) | — | — | — | 132·1 | 184·4 | 237·4 | 280·4 |

* See Rayleigh and Ramsay, 'Phil. Trans.,' 1895, A, p. 212.

The results of our observations are laid down in the table. In three cases (3, 4, and 6) the reading was taken at 0° , as well as at the boiling-point of water; this enabled us to calculate the coefficient of expansion between these two points. The result is shown in the fourth column. The higher temperatures determined with these thermometers have been derived from the observed pressures by using the coefficients thus measured. As the barometric pressures differed, more or less, from the normal value, the boiling-points had to be reduced to normal pressure, for which operation we made use of the differences in Ramsay and Young's well-known tables.* In calculating the temperatures of air thermometer I, where the reading at 0° had been omitted, and of argon thermometer II, where we did not take the reading in steam, we used the coefficients found with air thermometer II and argon thermometer I, respectively, in the first case basing our calculations on the reading in steam. With the hydrogen thermometer, where the reading at 0° had not been taken, we accepted 0.003663 as the coefficient of that gas, and based our calculations of the temperatures again on the reading in steam.

Since the readings of the mercury surfaces, with the gas thermometer as well as the barometer, were taken on a millimeter scale, an occasional mistake in the final pressure of 0.1 or 0.2 mm. is by no means excluded. Uncertainties of that amount do not, however, account for the differences between the results obtained with the different thermometers. The readings of air thermometer I are, perhaps, somewhat less to be relied upon than the others, because they had to be observed, as was stated above, by one of us in the absence of the other. The boiling-point of bromnaphthalene, as determined with the helium thermometer, is also very uncertain, because the position of the mercury was not at all stable, probably on account of the difficulty of obtaining rapid and smooth boiling of the liquid. Yet, even if these values are not taken into account, the differences are very remarkable, especially with quinoline, and the agreement with Wiebe's result is also not quite satisfactory. Part of these differences may be due to impurity in the liquids used in the jacket. Pains were taken at the beginning of our experiments to have them quite pure, but as the values show, apparently, a tendency to rise, it may be that continuous boiling produced slight decomposition. In the case of bromnaphthalene this is more than possible. If more time had been at our disposal, we should have tested the purity of our substances during the operations. As it is now, it would be unwise to draw conclusions from our figures about the exact behaviour of any of the gases used at high temperatures. The coefficients of expansion between 0° and 100° found for argon and helium agree very well with the values usually found for gases, and there is no

* 'Chem. Soc. Journ.,' vol. 47, p. 640; vol. 55, p. 483.

indication of anything extraordinary happening to these gases at high temperatures. When argon thermometer I was heated in the vapour of quinoline a remarkable expansion of the gas was observed, continuing for two hours until a maximum value was reached; this gave an apparent temperature of 243.5° for the boiling point of quinoline. On cooling the thermometer, however, it was found to be cracked, and some drops of quinoline were noticed inside the bulb. The measurements made in this case were therefore rejected, and a new series was begun with argon thermometer II, which gave a value about normal. How the quinoline could have found its way into the bulb while an interior pressure of about 970 mm. existed within it, without the argon escaping rapidly at the same time, is not quite clear. It may be the vapour passed through the crack when the temperature was rather low, and that the opening was closed by the later expansion of the glass.

For completeness' sake, we give in the table the boiling-points of the same substances determined with a mercury thermometer, as calculated from Ramsay and Young's tables. But the irregularities of the thermometers prevent our giving any definite numbers for the reduction of those tables to accord with any of the gas thermometer scales. A direct comparison, such as was executed by Wiebe and Böttcher with a mercury thermometer of known constitution, like the Jena glass thermometer, would have been desirable. Differences of boiling-point resulting from impurities would have affected both thermometers in the same way, and would have enabled us to ascertain how much of the differences found resulted from that source of error. But here also want of time prevented our extending our programme beyond the limits fixed beforehand.

Notwithstanding the incompleteness and want of perfection of our work, we do not hesitate to publish our results: the difficulties to be overcome in experiments of this kind are serious, and we did not make it our object to obtain results of remarkable accuracy. The real motive of the work was to discover whether argon and helium show extraordinary behaviour at high temperatures, or not—and our results apparently establish the fact that they do not. Their behaviour, so far as expansion is concerned and within the limits of temperature which we used, is apparently the same as that of so-called perfect gases or mixtures of them.

Finally, it is a great pleasure to record our hearty appreciation of the kindly assistance of Professor Ramsay, at whose suggestion, and under whose supervision, these experiments have been conducted.